



Faculty of Resource Science and Technology

**Distribution and Source of Hydrocarbons in Marine Sediments from
Exclusive Economic Zone (EEZ) off Sarawak, Malaysia.**

Nooraini binti Lai Budi

**Master of Science
2019**

Distribution and Source of Hydrocarbons in Marine Sediments from
Exclusive Economic Zone (EEZ) off Sarawak, Malaysia

Nooraini binti Lai Budi

A thesis submitted

In fulfilment of the requirements for the degree of Master of Science

(Environmental Chemistry)

Faculty of Resource Science and Technology
UNIVERSITY MALAYSIA SARAWAK
2019

DECLARATION

I declare the work in this thesis was carried out in accordance with the regulations of University Malaysia Sarawak. The thesis is original and it is the result of my work, unless otherwise indicated or acknowledged as reference work. The thesis has not been accepted for any degree and is not currently submitted in candidature for any other degree.

Nooraini binti Lai Budi

Faculty of Resource Science and Technology

Universiti Malaysia Sarawak

Date:

ACKNOWLEDGMENT

I would like to express my greatest thankfulness to my supervisor, Professor Dr Zaini Bin Assim and my co-supervisor, Professor Dr Fasihuddin Badruddin Ahmad for their guidance and support throughout this project. I would also like to express my gratitude to the following laboratory assistants of the Department of Chemistry, Faculty of Resource Science and Technology, Mr. Rajuna, Madam Dayang Fatimawati, and Mr Benedict Samling who always helping me during my project lab work and not forgetting my friends, Nadia binti Mat, Nurul Afina binti Sumed and Peggy Ngu who always help and give moral support. Finally, I would also like to express my appreciation to my beloved parents Lai Budi Mustapha and Hasnah Abdullah @ Lanchang ak Gimam and my beloved family for their love, encouragement and support throughout the duration of my study.

ABSTRACT

The concentration and sources of aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) in surface and core sediments from Sarawak Exclusive Economic Zone (EEZ) were investigated. Aliphatic hydrocarbons concentrations in surface sediments ranged between 2.8-744.4 µg/g. The highest concentration of total aliphatic hydrocarbons (TAHs) was detected in surface sediment of ST02 (Kuching Waters) with 744.4 µg/g. Concentration of aliphatic hydrocarbons in core sediments ranged between 7.0-123.7, 122.6-324.4 and 8.05-46.6 µg/g of ST01, ST02 and ST03, respectively. The sources of aliphatic hydrocarbons in sediments of Sarawak EEZ were originated from mixture of anthropogenic and biogenic sources as indicated by alkane biomarker indices. Fresh oil input has been detected in sediments at several sites of Sarawak EEZ whereas old petroleum contamination also being observed as indicated by presence of unresolved complex mixture (UCM) and hydrocarbon biomarkers (hopane and sterane). Concentrations of PAHs in surface sediments of Sarawak EEZ ranged 8.56-374.7 ng/g. Several sites at Sarawak EEZ were moderately polluted by PAHs but the PAHs concentrations did not pose biological adverse effects because not exceeded the effect range low (ERL) and effect range medium (ERM). Isomeric PAHs ratios were employed to determine sources of PAHs in sediments from Sarawak EEZ. The main source of PAHs in surface sediments of Sarawak EEZ as indicated by Principal Component Analysis (PCA) was pyrogenic. The dominance of high molecular weight (4,5 and 6 ring) PAHs in surface sediments of Sarawak EEZ were correlated with silt and clay fractions. Concentrations of PAHs in core sediments of ST01, ST02 and ST03 were 13.6-92.5, 37.2-151.2 and 24.3-72.9 ng/g, respectively. The presence of unweathered fresh petroleum source was detected in core sediment of ST01. PAHs origin in core sediment of

ST02 were believed from mixture of pyrogenic and petrogenic with minor input of pyrolytic PAHs. Source of PAHs in core sediment of ST03 was mainly derived from combustion (pyrogenic).

Keywords: Aliphatic hydrocarbons; polycyclic aromatic hydrocarbons (PAHs), heavy metals, sediments; Sarawak Exclusive Economic Zone (EEZ).

***Taburan dan Sumber Hidrokarbon dalam
Enapan Marin dari Zon Ekonomi Eksklusif Sarawak, Malaysia***

ABSTRAK

Kepekatan dan sumber hidrokarbon alifatik dan hidrokarbon aromatic polisiklik (HAP) dalam sedimen permukaan dan sedimen teras dari Zon Eksklusif Ekonomi (ZEE) Sarawak telah dikaji. Kepekatan hidrokarbon alifatik dalam sedimen permukaan adalah dalam 2.8-744.4 µg/g dengan kepekatan total hidrokarbon alifatik tertinggi dikesan dalam sedimen permukaan ST02 (Perairan Kuching) dengan 744.4 µg/g. Kepekatan hidrokarbon alifatik dalam sedimen teras masing-masing adalah dalam julat 7.0-123.7, 122.6-324.4 dan 8.05-46.6 µg/g di ST01, ST02 dan ST03. Sumber hidrokarbon alifatik dalam sedimen dari ZEE Sarawak adalah berasal dari campuran antropogenik dan biogenik seperti yang ditunjukkan oleh index penanda biologi alkana. Input minyak yang baru telah dikesan dalam sedimen pada beberapa tempat di ZEE Sarawak manakala pencemaran minyak lama juga diperhatikan seperti ditunjukkan oleh kehadiran campuran kompleks tidak terurai dan penanda biologi hidrokarbon (hopana dan sterana). Kepekatan HAP dalam sedimen permukaan ZEE Sarawak adalah dalam julat 8.56-374.7 ng/g. Beberapa lokasi pensampelan di ZEE Sarawak adalah sederhana tercemar oleh HAP tetapi kepekatan HAP tidak menyebabkan kesan buruk biologi kerana tidak melebihi kesan julat rendah dan kesan julat sederhana. Nisbah isomer HAP telah digunakan untuk menentukan sumber HAP dalam sedimen dari ZEE Sarawak. Sumber utama HAP dalam sedimen permukaan seperti ditunjukkan oleh Analisis Komponen Prinsipal (AKP) adalah sumber pirogenik. HAP dengan berat molekul tinggi (4, 5 dan 6 gelang) adalah dominan dalam sedimen permukaan di ZEE Sarawak dan berkorelasi dengan pecahan lodak dan tanah liat. Kepekatan HAP dalam sediment teras dari ST01, ST02 and ST03 masing-masing adalah dalam julat 13.6-

92.5, 37.2-151.2 and 24.3-72.9 ng/g. Kehadiran petroleum baru tidak terluluhawa telah dikesan dalam sedimen teras pada ST01. Sumber HAP dalam sedimen teras ST02 dipercayai dari campuran pirogenik dan petrogenik dengan input minor HAP pirolitik. Sumber HAP dalam sediment teras ST03 adalah datang dari pembakaran (pirogenik).

Kata kunci: Hidrkarbon alifatik; hidrokarbon aromatik polisiklik; sedimen; Zon Eksklusif Ekonomi Sarawak.

TABLE OF CONTENTS

	Page
DECLARATION	i
ACKNOWLEDGEMENT	ii
ABSTRACT	iii
<i>ABSTRAK</i>	v
TABLE OF CONTENTS	vii
LIST OF TABLES	xii
LIST OF FIGURES	xiv
LIST OF ABBREVIATIONS	xvi
CHAPTER 1: INTRODUCTION	1
1.1 General Introduction	1
1.2 Problem Statement	3
1.3 Objectives of the study	3
CHAPTER 2: LITERATURE REVIEW	4
2.1 Exclusive Economic Zone of Malaysia	4
2.2 The Concept of Exclusive Economic Zone (EEZ)	5
2.3 Hydrocarbons Studies in Malaysia	6
2.4 Significant Study of Hydrocarbons in Marine Sediments of Malaysia	9
2.5 Aliphatic Hydrocarbons	11
2.5.1 Occurrence of Aliphatic Hydrocarbon in Marine Sediment	11

2.5.2	Source Identification of Hydrocarbons Using <i>n</i> -Alkane Molecular Marker	12
2.5.2.1	<i>n</i> -Alkanes Characteristics	12
2.5.2.2	Carbon Preference Index (CPI)	13
2.5.2.3	Major Hydrocarbons	14
2.5.2.4	Low Molecular Weight to High Molecular Weight Ratio (LMW/HMW)	15
2.5.2.5	Unresolved Complex Mixture (UCM)	15
2.5.2.6	Average Chain Length (ACL)	15
2.5.2.7	Isoprenoids (Pristane to Phytane ratio, Pr/Ph)	16
2.6	Polycyclic Aromatic Hydrocarbons (PAHs)	17
2.6.1	Sources of PAHs	17
2.6.2	Physical and Chemical Properties of PAHs	18
2.6.3	Effect of PAHs Towards Organisms	22
CHAPTER 3: MATERIALS AND METHODS		24
3.1	Area of Sampling and Field Sampling	24
3.2	Proximate and Grain Size Analysis	27
3.2.1	Proximate Analysis	27
3.2.2	Grain Size Analysis	28
3.3	Determination of Hydrocarbons in Marine Sediment of Sarawak EEZ	29
3.3.1	Extraction and Fractionation of Hydrocarbons in Sediments	29
3.3.2	Gas Chromatographic Analyses	31

3.3.2.1	Gas Chromatography-Flame Ionization Detector (GC-FID)	
	Analysis	31
3.3.2.2	Gas Chromatography-Mass Spectrometry (GC-MS)	
	Analysis	32
3.3.3	Quantitative and Qualitative Analysis of <i>n</i> -alkanes and PAHs	32
3.3.3.1	Quantitative Analysis of <i>n</i> -Alkanes and PAHs	32
3.3.3.2	Qualitative Analysis	34
3.3.4	Determination of Hydrocarbon Molecular Indices	34
3.3.4.1	Carbon Preferences Index (CPI)	34
3.3.4.2	Average Chain Length (ACL)	35
3.3.4.3	Low Molecular Weight to High Molecular Weight Ratio (LMW/HMW)	35
3.3.4.4	Terrigenous Aquatic Ratio (TAR)	36
3.3.4.5	Isoprenoid Ratios	36
3.3.4.6	Unresolved complex mixture (UCM)	37
3.3.5	Environmental Evaluation Method of PAHs	37
3.3.5.1	Sediments Quality Guidelines (SQGs)	37
3.5	Statistical Analysis	38
3.5.1	Correlation Analysis	39
3.5.2	Principal Component Analysis (PCA)	39
3.5.3	Cluster Analysis (CA)	39

CHAPTER 4: RESULTS AND DISCUSSION	40
4.1 Grain Size Distribution and Proximate Data of Sediment	40
4.2 Aliphatic Hydrocarbons in Marine Sediments of Sarawak's EEZ	42
4.2.1 Aliphatic Hydrocarbons Standard	42
4.2.2 Aliphatic Hydrocarbons in Surface Sediments of Sarawak EEZ	44
4.2.3 Sources Identification of Aliphatic Hydrocarbons Using <i>n</i> -Alkane Molecular Marker in Surface Sediment of Sarawak EEZ	51
4.2.3.1 Carbon Preferences Index (CPI) and Ratios of Isoprenoid Hydrocarbons	52
4.2.3.2 Ratio of Low Molecular Weight to High Molecular Weight (LMW/HMW)	53
4.2.3.3 Average Chain Length (ACL) and The Terrigenous/Aquatic Ratio (TAR)	54
4.2.3.4 Unresolved Complex Mixture (UCM)	55
4.2.4 Aliphatic Hydrocarbons in Core Sediments of Sarawak EEZ	57
4.2.5 Sources Identification of Aliphatic Hydrocarbons Using <i>n</i> -Alkane Molecular Marker in Core Sediment of Sarawak EEZ	59
4.2.5.1 Carbon Preferences Index (CPI) of <i>n</i> -alkane in Core Sediments	59
4.2.5.2 Ratio of Low Molecular Weight to High Molecular Weight (LMW/HMW) of <i>n</i> -alkane in Core Sediments	62
4.2.5.3 Ratios of Isoprenoid Hydrocarbons in Core Sediments	63
4.2.6 Aliphatic Hydrocarbon Biomarkers	65
4.2.6.1 Pentacyclic Triterpanes	65

4.2.6.2	Sterane Fingerprinting	66
4.2.7	Summary on Aliphatic Hydrocarbons in Marine Sediments of Sarawak EEZ	68
4.3	Polycyclic Aromatic Hydrocarbons (PAHs) in Marine Sediments of Sarawak's EEZ	69
4.3.1	Response Factor of Individual PAH in Standard Mixture	69
4.3.2	Distribution of PAHs in Marine Surface Sediments	70
4.3.3	Possible Source of PAHs in Surface Sediment from Sarawak EEZ	78
4.3.4	Ecological Risk of PAHs in Surface Sediments of Sarawak EEZ	81
4.3.5	Distribution of Polycyclic Aromatic Hydrocarbons from Other Regions	83
4.3.6	Distribution of PAHs in Core Sediments from Sarawak EEZ	85
4.3.7	Possible Source of PAHs in Core Sediment from Sarawak EEZ	90
4.3.8	Principal Component Analysis (PCA) of Hydrocarbons in Surface Sediment from Sarawak EEZ	95
4.3.9	Cluster Analysis (CA) on Hydrocarbons in Surface Sediments of Sarawak EEZ	98
4.3.10	Summary on PAHs in Marine Sediments of Sarawak EEZ	101
CHAPTER 5: CONCLUSIONS AND RECCOMENDATIONS		102
5.1	Conclusions	102
5.2	Recomendations for Future Study	103
REFERENCES		104
APPENDICES		129

LIST OF TABLES

		Page
Table 2.1	Hydrocarbons concentrations in sediments from offshore water (South China Sea) surveyed during Matahari Expedition and SEAFDEC	8
Table 2.2	Concentrations of petroleum hydrocarbons (mg/kg) in coastal sediments from several locations in in Malaysia.	8
Table 2.3	Respective inputs of <i>n</i> -Alkane based on CPI ratios	14
Table 2.4	General use of PAHs in certain industries	19
Table 2.5	Physical and chemical properties of PAHs compounds	20
Table 3.1	GPS reading and characteristics of sampling sites at Sarawak's EEZ	26
Table 3.2	Fractionation of geolipid on silica gel column chromatography with respective eluting solvents	30
Table 3.3	Toxicity guideline for individual PAH ranged for ERL and ERM	38
Table 4.1	Percentage of Particle Sizes of Surface Sediment of Sarawak EEZ	41
Table 4.2	Proximate analysis of surface sediments of Sarawak's EEZ	41
Table 4.3	Correlation Analysis of sediment fractions with TOM and Ash	42
Table 4.4	Retention time and response factor of individual <i>n</i> -alkanes and isoprenoids	43
Table 4.5	Concentration of aliphatic hydrocarbons (µg/g dry weight) in surface sediments from Sarawak's Exclusive Economic Zone	49
Table 4.6	Molecular indices of <i>n</i> -alkanes from surface sediments from Sarawak EEZ	51
Table 4.7	<i>n</i> -Alkanes ranged for bimodal in GC-FID chromatograms	56
Table 4.8	Concentrations of TAH (ug/g) and molecular index of alkanes in each layers of core sediment from ST01, ST02 and ST03	61
Table 4.9	Retention times and relative response factors for 14 PAHs standard using d ₁₀ anthracene as internal standard	70

Table 4.10	Individual concentration (ng/g) of PAHs in surface sediments from Sarawak EEZ	77
Table 4.11	Sources of PAHs in Marine Surfaces Sediment Based on Isomeric Pair Ratio	80
Table 4.12	Sediment quality guidelines (SQGs) for PAHs in surface sediment of Sarawak EEZ	82
Table 4.13	Distirbution of PAHs from Other Areas	84
Table 4.14	Eigenvalues, percentage variance and total variance of hydrocarbons in surface sediments	96
Table 4.15	PCA of hydrocarbons in surface sediments from Sarawak EEZ	97
Table 4.16	The agglomeration schedule for hydrocarbons in studied surface sediments from Sarawak EEZ	100

LIST OF FIGURES

		Page
Figure 3.1	Sampling stations of surface and core sediments at Sarawak EEZ	25
Figure 4.1	GC-MS chromatogram of mixture of <i>n</i> -alkane standard	42
Figure 4.2	GC-MS chromatogram of aliphatic fraction in surface sediment of ST01, ST02 and ST03	45
Figure 4.3	GC-MS chromatogram of aliphatic fraction in surface sediment of ST04, ST05 and ST06	46
Figure 4.4	GC-MS chromatogram of aliphatic fraction in surface sediment of ST07, ST08 and ST09	47
Figure 4.5	GC-MS chromatogram of aliphatic fraction in surface sediment of ST10 and ST11	48
Figure 4.6	GC-FID chromatograms of aliphatic hydrocarbons in layer 2.5-5.0 cm in core sediments of ST01, ST02 and ST03	58
Figure 4.7	Vertical trend of CPI in core sediment ST01, ST02 and ST03	60
Figure 4.8	Vertical profile of LMW/HMW of <i>n</i> -alkanes in core sediment at ST01, ST02 and ST03	63
Figure 4.9	Vertical profile of C ₁₇ to Pristane (C ₁₇ /Pr) in core sediment ST01, ST02 and ST03	64
Figure 4.10	Vertical profile of C ₁₈ to phytane (C ₁₈ /Ph) in core sediment ST01, ST02 and ST03	64
Figure 4.11	Mass chromatogram of hopane series (m/z 191) in aliphatic fractions from surface sediments in station ST06 of Sarawak EEZ	66
Figure 4.12	Mass chromatograms of steranes (m/z 217) in aliphatic fraction from surface sediments in station ST04 of Sarawak EEZ	67
Figure 4.13	GC-FID chromatogram of 14 components of PAHs standard	69
Figure 4.14	GC-FID traces for PAH from surface sediment at ST01, ST02 and ST03	73
Figure 4.15	GC-FID traces for PAH from surface sediment at ST04, ST05 and ST06	74

Figure 4.16	GC-FID traces for PAH from surface sediment at ST07, ST09 ST10 and ST11	75
Figure 4.17	GC-FID traces for PAH from surface sediment at ST11	76
Figure 4.18	The percentage of compositional pattern for unsubstituted PAHs in surface sediments from Sarawak EEZ	76
Figure 4.19	GC-FID chromatogram of PAH in layer 2.5-5.0 cm of core sediments from ST01, ST02 and ST03 of Sarawak EEZ	87
Figure 4.20	Vertical profile Σ PAHs in core sediment ST01, ST02 and ST03	88
Figure 4.21	Percentage (%) Composition of Ring Size in Core Sediment from ST01, ST02 and ST03	89
Figure 4.22	Vertical trend for LMW/HMW PAHs in core sediment ST01, ST02 and ST03	92
Figure 4.23	Vertical trend for Anth/(Anth+Phe) ratios in core sediment ST01, ST02 and ST03	92
Figure 4.24	Vertical trend for Fluo/(Fluo+Pyr) ratios in core sediment ST01, ST02 and ST03	94
Figure 4.25	Vertical trend for BaA/(BaA+Chr ratios in core sediment ST01, ST02 and ST03	94
Figure 4.26	PCA score plot that accounting for 70% of total variance from hydrocarbons data in surface sediments	96
Figure 4.27	Hierarchical cluster analysis on hydrocarbons in surface sediments	99

LIST OF ABBREVIATIONS

ACL	Average Chain Length
B[a]A	Benzo[a]anthracene
B[b]F	Benzo[b]fluoranthene
B[ghi]P	Benzo[ghi]perylene
B[k]F	Benzo[k]fluoranthene
CPI	Carbon Preferences Index
DB[b]A	Dibenz[a,h]anthracene
EEZ	Economic Exclusive Zone
ERL	Effect Range Low
ERM	Effect Range Medium
GC-FID	Gas Chromatography-Flame Ionization Detector
GC-MS	Gas Chromatography-Mass Spectrometry
HMW	High Molecular Weight
I _{geo}	Geochemical Accumulation Index
IS	Internal Standard
LMW	Low Molecular Weight
m/z	Mass-to-Charge Ratio
PAHs	Polycyclic Aromatic Hydrocarbons
PCA	Principal Component Analysis
PEL	Probable Effect Limit
SEAFDEC	Southeast Asian Fisheries Development Center
SQGs	Sediment Quality Guidelines

TAH	Total Aliphatic Hydrocarbons
TAR	Terrigenous/Aquatic Ratio
TEL	Threshold Effect Limit
TOM	Total Organic Matter
UCM	Unresolved Complex Mixture
UNCLOS	United Nations Convention on the Law
US EPA	United States Environmental Protection Agency

